



## Endosulfan wet deposition in Southern Florida (USA)



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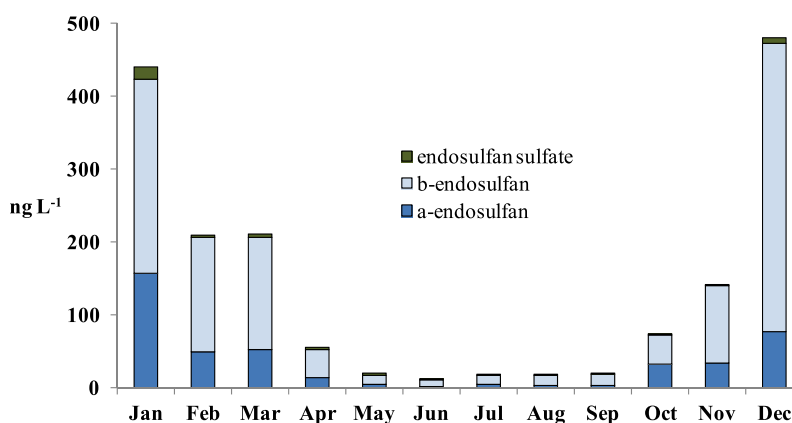
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### HIGHLIGHTS

- Endosulfan measured in rain for 4 years at three sites in Southern Florida
- High concentrations and wet deposition rates found within an area of high use
- Everglades and Biscayne National Parks border use areas
- Atmospheric transport to and wet deposition within these parks observed
- Potential for adverse ecological impact was indicated.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The atmosphere is an important transport route for semi-volatile pesticides like endosulfan. Deposition, which depends on physical–chemical properties, use patterns, and climatic conditions, can occur at local, regional, and global scales. Adverse human and ecological impact may result. We measured endosulfan wet deposition in precipitation over a 4-year period within an area of high agricultural use in Southern Florida (USA) and in nearby Biscayne and Everglades National Parks. Endosulfan's two isomers and degradate, endosulfan sulfate, were detected at high frequency with the order of detection and concentration being  $\beta$ -endosulfan >  $\alpha$ -endosulfan > endosulfan sulfate. Within the agricultural area, detection frequency (55 to 98%) mean concentrations (5 to 87 ng L<sup>-1</sup>) and total daily deposition (200 ng m<sup>-2</sup> day<sup>-1</sup>) exceeded values at other sites by 5 to 30-fold. Strong seasonal trends were also observed with values at all monitored sites significantly higher during peak endosulfan use periods when vegetable crops were produced. Relatively high deposition in the crop production area and observations that concentrations exceeded aquatic life toxicity thresholds at all sites indicated that endosulfan volatilization and wet deposition are of ecotoxicological concern to the region. This study emphasizes the need to include localized volatilization and deposition of endosulfan and other semi-volatile pesticides in risk assessments in Southern Florida and other areas with similar climatic and crop production profiles.

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## 1. Introduction

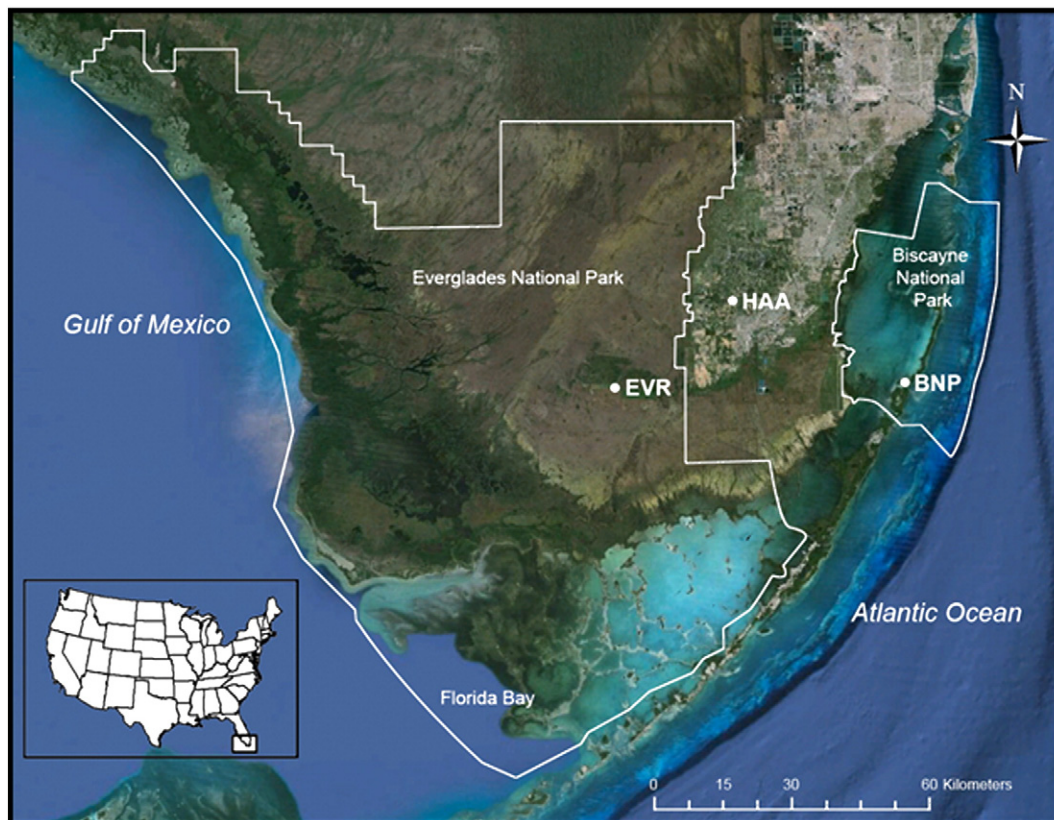
After more than six decades of intensive use, endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide) continues to be an effective insecticide. The technical product is a mixture of two diastereoisomers known as  $\alpha$ -endosulfan (or I) and  $\beta$ -endosulfan (or II) with  $\alpha$ - and  $\beta$ -isomers typically in a 70:30 ratio, respectively. Endosulfan is valued for control of many crop damaging pests, potential for use in rotation with other insecticides for resistance management and for its relatively low cost and toxicity to pollinators (U.S.EPA, 2002; Janssen, 2011). Notably, neonicotinoid insecticides that are increasingly used in place of endosulfan are highly toxic to bees and have been implicated in the decline of bee populations in the USA and Europe (EFSA, European Food Safety Authority, 2013).

Recent risk assessments have indicated that likely exposures to both endosulfan isomers and endosulfan sulfate, through normal use in crop production, present unacceptably high risks to farm workers and wildlife (UNEP-POPRC, 2009; U.S.EPA, 2010a). In most studies, the three forms are considered to be equivalent in terms of potential toxic impact and are summed to evaluate exposure risk (Weber et al., 2010). This sum is identified as “total endosulfans” in discussions that follow. Other concerns linked to exposure potential are endosulfan atmospheric transport, persistence of the parent isomers and degradate endosulfan sulfate in soil, water, and sediment, and bioaccumulation (UNEP-POPRC, 2009). These issues led to the classification of endosulfan as a persistent organic pollutant by the Stockholm Convention on Persistent Organic Pollutants and to plans for phased termination of all uses globally (UNEP-POP, 2011). The Convention agreement terminated most endosulfan uses in 2012. India was granted an exemption for use of 14 crops until 2017. Continued use of selected crops in China, at least until mid-2016, is also anticipated (U.S.EPA, 2013).

In the USA, an earlier agreement defined plans to terminate all endosulfan uses by the end of 2016 and within the highest use state, Florida, in 2014 (U.S.EPA, 2010a). USDA data collected in, 2011 indicated that endosulfan use in Florida accounted for more than 50% of all uses nationwide. A very high use area is around the city of Homestead in the southern-most part of the state (Fig. 1). An estimated six to eleven metric tons are applied annually to the approximately 14,000 ha in vegetable and nursery crop production in Homestead's agricultural area (HAA) (Stone, 2013). HAA is surrounded by Everglades National Park (EVR) on the west and south, Biscayne National Park (BNP) on the east, and the urbanized area of southern Miami on the north (Fig. 1). Environmental monitoring within HAA over the past two decades has documented the presence of endosulfan residues in surface water, sediment, and biota (Fulton et al., 2004; Harman-Fetcho et al., 2005; Pfeuffer, 2011; U.S.EPA, 2010a). Data have indicated potential for adverse ecological impact to freshwater and marine ecosystems (Fulton et al., 2004; Rand et al., 2010; Scott et al., 2002).

A principal concern is endosulfan's high toxicity to aquatic organisms. Water quality criteria established by U.S. EPA (2012) for protection of the most sensitive freshwater indicator species are 0.220 and 0.056  $\mu\text{g L}^{-1}$  for acute and chronic exposures respectively. The corresponding criteria for marine species are 0.034 and 0.0087  $\mu\text{g L}^{-1}$ . Bioaccumulation has also been observed. Endosulfan and the toxic degradate, endosulfan sulfate, were detected in tissues of small demersal fish in Southern Florida at levels that may adversely impact wading birds and other organisms that use these fish as food sources (Rand et al., 2010). Since residues were found in fish captured in areas that were not adjacent to land used for crop production, a link to endosulfan atmospheric transport and deposition was indicated.

These findings motivated our effort to evaluate atmospheric transport and wet deposition of endosulfan's two isomers and endosulfan sulfate within the HAA and the National Parks. A summary of ground



**Fig. 1.** National Park boundaries and locations of wet-deposition collectors in the Homestead Agricultural Area (HAA), Everglades National Park (EVR), and Biscayne National Park (BNP) (Google Earth, 2013).

level air sample measurements taken over 5 years was recently published (Hapeman et al., 2013). When compared to other published data total endosulfan concentration in HAA air was very high, exceeding most values by 10 to 1000-fold (e.g. Burgoyne and Hites, 1993; Li et al., 2012; Meire et al., 2012; Pozo et al., 2009; Weber et al., 2010; Yao et al., 2006). Air concentrations were comparable to those observed in samples collected during a survey of endosulfan gas phase concentrations in agricultural areas of India where endosulfan was used intensively (Pozo et al., 2011).

A mechanism for endosulfan removal from the atmosphere is precipitation scavenging. Wet deposition measurements have been described in many studies (Carrera et al., 2002; Chan et al., 1994; Chan et al., 2003; Gioia et al., 2005; Goel et al., 2005; Kuang et al., 2003; Laabs et al., 2002; McConnell et al., 1998; Quaghebeur et al., 2004; Tuduri et al., 2006; Wong et al., 2004). Detection of both endosulfans, and in some cases endosulfan sulfate, was observed. Trends in concentration were typically  $\beta$ -endosulfan >  $\alpha$ -endosulfan > endosulfan sulfate. The highest concentrations and deposition rates were near the areas of endosulfan use in Brazil (Laabs et al., 2002); total endosulfans' maximum concentrations and deposition were  $1.1 \mu\text{g L}^{-1}$  and  $1.5 \mu\text{g m}^{-2} \text{day}^{-1}$ , respectively. Observations in other studies reflected medium and long-range transport with corresponding concentration and deposition rates of 100 to 1000-fold less (Weber et al., 2010). Few studies have been conducted within endosulfan use areas thus little is known about the rate and extent of volatilization and re-deposition in these areas.

Here we describe the concentration, distribution of isomers, and spatial and temporal variance of endosulfan and endosulfan sulfate in precipitation over a two to four year period, 2002–2006 at three sites with one each in the HAA (39 months), EVR (28 months), and BNP (46 months). We also report wet deposition and compare findings to published water quality data and acute and chronic water quality criteria for the protection of aquatic life.

## 2. Materials and methods

### 2.1. Study area and sample collection locations

Sampling locations, HAA (25.5087750, 80.4987111), EVR (25.3903806, 80.6799778), and BNP (25.3975139, 80.2346333) were described by Hapeman et al. (2013) (Fig. 1). The HAA site was located near the Homestead Florida Agricultural Weather Network (FAWN) weather station (FAWN, 2013). In areas about 0.5 km from this site, intensive commercial vegetable crop production during winter months (October through March) includes: tomatoes (*Solanum lycopersicum*), snap beans (*Phaseolus vulgaris*), eggplant (*Solanum melongena*), and other crops that were likely to be treated with endosulfan to control white fly (*Bemisia argentifolii*) and other pests. The EVR site was within the boundaries of the park at the Daniel Beard Research Center and was about 10 km south-west of agricultural fields commonly-used for tomato production. The site was surrounded by grasses, shrubs, and trees. The BNP site was located on Adams Key, a small island surrounded by the Atlantic Ocean on the east and Biscayne Bay on the west. BNP is more than 20 km east of most agricultural activities.

### 2.2. Rain sample collection

Event-based rain samples were collected using a modified MIC-B® rain sampler (Meteorologic Instruments of Canada, Richmond, ONT, Canada) equipped with a covered  $0.2 \text{ m}^2$  stainless steel funnel and lid controlled by moisture activated sensor. Attached to the bottom of the funnel was a filter cartridge assembly composed (sequentially) of the following: a Teflon® column (12 cm length  $\times$  14 mm diameter), a Teflon® filter head containing a 45-mm diameter glass fiber filter (Whatman GF/F,  $0.7 \mu\text{m}$  nominal pore size), and a solid phase extraction (SPE) cartridge containing 500 mg of Oasis® HLB copolymer beads (Waters, USA). A peristaltic pump was connected to the cartridge outlet,

which was activated when the funnel lid was opened, and pulled rainwater through the filter cartridge assembly at a flow rate of  $20\text{--}50 \text{ mL min}^{-1}$ . The extracted water was collected in a 20-L carboy for volume measurement. Each event was defined as any rain that fell during a 24-h period from 10 AM to 10 AM ( $\pm 1 \text{ h}$ ) the following day and yielded greater than 100 mL (0.5 mm). After events, cartridges and filters were removed, the funnel was cleaned with 4 to 6 L of 50% methanol in distilled-deionized water, and cartridges and filters were replaced. Exposed cartridges were dried with high purity nitrogen gas, stored at  $-20^\circ\text{C}$ , and shipped to the USDA-ARS, Southeast Watershed Laboratory, Tifton, GA (USA) for elution and analysis.

HAA site collections were from Jan-2003 to Mar-2006, BNP from Nov-2002 to Aug-2006, and EVR from Apr-2004 to Jul-2006. Comparison of the sample volume collected at HAA to the amount of precipitation recorded by the FAWN system (FAWN, 2013) indicated 70% collection efficiency for the sampler. Rain capture rates were comparable to values reported in other studies (Carrera et al., 2002). Inspection of the precipitation record indicated that 60% of the rainfall not recorded by rain sampler came in large tropical storm events. Typically electrical power loss during events disabled the sampler. In other cases when rain was greater than 93 mm in 24-h, the internal reservoir was overfilled.

### 2.3. Sample processing and analysis

SPE cartridges were eluted sequentially with 3 mL methanol and methylene chloride. Combined eluents were concentrated under an  $\text{N}_2$  gas stream to 1 mL. Solvent exchange to toluene using a TurboVap® concentrator (Biotage, LLC, Charlotte, NC, USA) and adjustment to 1 mL followed. Extracts were fortified with 25 ng octafluoronaphthalene (OFN) which was used as an internal standard and analyzed for  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate, by gas chromatography-methane negative chemical ionization mass spectrometry using a DSQII Thermoquest-Finnigan GC/MS system (ThermoFisher Scientific, San Jose, CA, USA). The GC column was a 30 m DB5MS® column (Agilent, Santa Clara, CA, USA), with inner diameter of 0.25 mm and film thickness of  $0.25 \mu\text{m}$ . Helium carrier gas flow was fixed at  $2 \text{ mL min}^{-1}$ . Injections were in the splitless mode at  $220^\circ\text{C}$  with pressure surged to 250 kPa for 1 min after injection. Column oven temperature at injection,  $80^\circ\text{C}$ , was held for 1 min then increased to  $260^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$  and held for 2 min. Methane flow was  $1.5 \text{ mL min}^{-1}$  and source temperature was  $200^\circ\text{C}$ . Prior to use the mass spectrometer was autotuned to meet PFTBA ion abundance and ratio criteria were specified by the manufacturer. Data acquisitions were in the selected ion monitoring mode. Ions monitored were  $m/z = 254$ , **272** (OFN); **242**, **406**, **408** ( $\alpha$ -endosulfan); **242**, **406**, **408** ( $\beta$ -endosulfan); and **352**, **386**, **388** (endosulfan sulfate). Ions in bold italics were used for quantitation. Confirmation criteria included retention time within  $\pm 0.05 \text{ min}$ , detection of all target ions, and the relative response ratio between the quantitation ion and the next most abundant ion within  $\pm 20\%$  of the analytical standard. The method detection limit (MDL) in sample extracts,  $2 \text{ ng mL}^{-1}$  translated to rain sample detection limits ranging from 0.1 to  $20 \text{ ng L}^{-1}$  depending on sample volume. Analytical standards were purchased from Chem Service Inc. (West Chester, PA, USA). Optima® grade solvents were obtained from Thermo Fisher Scientific (Waltham, MA, USA).

### 2.4. Quality control

Equipment blanks were evaluated monthly at each site by processing 1 L of distilled-deionized water through the rain collectors. None of the target analytes were detected. Average (standard deviation) of analyte percent recovery from distilled-deionized water spikes was 108 (12), 99 (11), and 89 (5), for  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate, respectively.



## 2.5. Data analysis

Deposition was calculated by multiplying the measured sample volume times the corresponding concentration of each analyte. No corrections were made for events when samplers malfunctioned or the volume of rainfall exceeded the collection capacity of the sampler's internal reservoir. As noted above collection efficiency was about 70%. Deposition values were divided by the area of the sampler funnel opening (0.2 m<sup>2</sup>) to determine deposition per unit area (ng m<sup>-2</sup>). Estimates of daily deposition (ng m<sup>-2</sup> day<sup>-1</sup>) were computed by summing deposition for each event during selected periods and dividing by the consecutive number of days in the monitoring period. Where concentration measurements were <MDL, two approaches were taken: 1) zero was inserted for all values < MDL and 2) the MDL was inserted for all values < MDL. Contingency analyses of detection frequencies (Fisher's exact test) were performed using GraphPad Prism v. 5.0 (GraphPad Software, San Diego, CA, USA). The "box-and whisker" plot of the fraction of  $\alpha$ -endosulfan in samples was prepared with SigmaPlot™ 12.0 (SysStat Software Inc., San Jose, CA, USA). Estimates of means and medians based on Kaplan–Meier (KM) survival analyses were computed using the KM-stats v. 1.4 excel spreadsheet (Helsel, 2013). The KM method likely provided the most accurate estimates since all sample sets had relatively high percentages (>15%) of not detected values and there were multiple detection limits due to differences in sample volumes of rainfall events. While KM estimates are considered to be a robust method for datasets with large numbers of values below detection limits and multiple detection limits, there is potential for negative bias when the not detected values exceed 50% (EFSA, European Food Safety Authority, 2010). Tests for normality (Shapiro–Wilk) using Graph-pad Software indicated that datasets were not normally distributed. Thus, pair-wise comparisons of medians were made using the non-parametric Gehan's generalized Wilcoxon test available in ProUCL 4.1.00 statistical analysis software (U.S.EPA, 2010b). Significant differences were identified when  $p$  was <0.05. Other data analyses and manipulations were made with Excel 7.0 (Microsoft Corp., Redmond, WA).

## 3. Results and discussion

### 3.1. Concentration in rainfall by site

Detection frequencies for  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate, 76, 84, and 55%, respectively, were significantly higher in HAA than in EVR or BNP samples (Table 1). Corresponding detection frequencies of the three analytes in EVR samples, 23, 34, and 9% and BNP 12, 25, and 3% were not significantly different. In samples collected at the BNP site, the  $\beta$ -endosulfan detection frequencies were also significantly greater when compared to  $\alpha$ -endosulfan and endosulfan sulfate. In addition the detection frequency of  $\alpha$ -endosulfan was greater than that of endosulfan sulfate. The same patterns were observed with EVR and HAA samples with the exception that differences in detection frequencies for  $\beta$ -endosulfan were not significant.

Mean and median concentrations followed trends in detection frequency with the greatest values obtained with HAA samples followed in descending order by those collected at the EVR and BNP sites (Table 1). Comparison of medians showed that HAA sample  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and total endosulfans were significantly greater when compared to the other sites. The EVR was greater than BNP site medians; but only the difference in total endosulfans was significant. Endosulfan sulfate medians between these sites were not compared since not detected values exceeded 90% in the EVR and BNP sample sets (Table 1).

Pair-wise testing of within site data found that  $\beta$ -endosulfan median concentrations were significantly greater than  $\alpha$ -endosulfan and endosulfan sulfate medians in HAA samples. The median concentration of  $\beta$ -endosulfan was also significantly greater than the median concentration of  $\alpha$ -isomer in EVR and BNP sample sets. Again comparisons

**Table 1**

Summary statistics for  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate concentrations (ng L<sup>-1</sup>) during observation periods.

	$\alpha$ -Endosulfan	$\beta$ -Endosulfan	Endosulfan sulfate
<b>HAA (n = 214)</b>			
Detected (%)	76	84	55
Minimum detected	0.37	1.2	0.33
Maximum detected	740	2300	88
Mean $\pm$ std detected <sup>a</sup>	39 $\pm$ 91	100 $\pm$ 243	8.1 $\pm$ 14
KM mean $\pm$ std <sup>b</sup>	31 $\pm$ 81	87 $\pm$ 226	5.3 $\pm$ 11
KM median (25th to 75th percentiles) <sup>b</sup>	6.0 (2 to 23)	17 (5 to 71)	2.0 (1 to 4)
<b>EVR (n = 122)</b>			
Detected (%)	23	34	9
Minimum detected	0.33	0.23	0.51
Maximum detected	91	150	32
Mean $\pm$ std detected <sup>a</sup>	12 $\pm$ 21	19 $\pm$ 34	4.9 $\pm$ 9.0
KM mean $\pm$ std <sup>b</sup>	2.9 $\pm$ 11	6.9 $\pm$ 22	0.6 $\pm$ 3.2
KM median (25th to 75th percentiles) <sup>b</sup>	0 (0 to 0.6)	0.4 (0 to 2.6)	0 (0)
<b>BNP (n = 166)</b>			
Detected (%)	13	26	3
Minimum detected	0.12	0.21	1.1
Maximum detected <sup>a</sup>	28	85	2.6
Mean $\pm$ std detected	4.6 $\pm$ 7.5	8.7 $\pm$ 14	1.6 $\pm$ 0.65
KM mean $\pm$ std <sup>b</sup>	0.81 $\pm$ 3.3	2.6 $\pm$ 8.3	0.1 $\pm$ 0.51
KM median (25th to 75th percentiles) <sup>b</sup>	0.2 (0 to 0.4)	0.4 (0 to 1.8)	0 (0)

HAA = Homestead Agricultural Area; EVR = Everglades National Park; BNP = Biscayne National Park; number of samples shown in parenthesis.

<sup>a</sup> Mean  $\pm$  standard deviation of samples with measured concentration greater than the method detection limit.

<sup>b</sup> Mean  $\pm$  standard deviation and median based on Kaplan–Meier survival statistics with the insertion of method detection limits (Helsel, 2013).

were not made for EVR and BNP endosulfan sulfate medians due to high percentage of endosulfan sulfate not detected.

### 3.2. Comparison to air sample results

Patterns in sample detection and magnitudes of differences in means and medians were similar to patterns previously reported for air samples (Hapeman et al., 2013). A major difference between air and rain sample results was in relative concentrations of the endosulfan isomers. In air samples, the  $\alpha$ -endosulfan typically exceeded the  $\beta$ -endosulfan isomer concentration by 3 to 5 times (Hapeman et al., 2013). In rain samples  $\beta$ -endosulfan concentration exceeded the  $\alpha$ -endosulfan concentration by about 4-fold across all samples and sites. Greater  $\beta$ -endosulfan concentration when compared to  $\alpha$ -endosulfan has been reported in most studies when the two isomers were measured in rain samples and can be explained by relative differences in the isomers' gas phase washout ratios ( $W_G$ ) (Weber et al., 2010).  $W_G$  is typically defined as the concentration in rain divided by the concentration air (Wania et al., 1998). For endosulfan, focus on gas phase washout in deposition assessments was appropriate since air measurements showed that >99% of the  $\alpha$ -endosulfan and 89% of the  $\beta$ -endosulfan were in the gas phase (Hapeman et al., 2013).

When equilibrium partitioning is assumed a compound's  $W_G$  is equal to the product,  $R \cdot T$ , divided by its Henry's Law constant ( $H$ ) where  $R$  is the gas constant and  $T$  is the temperature in °K (Wania et al., 1998). Inserting  $H$  measured over 5 to 35 °C in deionized water (Cetin et al., 2006) for both compounds indicated that  $W_G$  is 14  $\pm$  1.7 times greater for  $\beta$ -endosulfan than  $\alpha$ -endosulfan over this temperature range. Thus, even though  $\alpha$ -endosulfan concentrations in air were 3 to 5 times higher than  $\beta$ -endosulfan,  $\beta$ -endosulfan was strongly enriched in rain samples due higher  $W_G$ . As noted by Wania et al. (1998) several studies have shown that equilibrium between gas phase organic pollutants and rain may be achieved by the time it takes a raindrop to fall a few meters, however exceptions were reported. The most common was when dissolved concentrations greater than predicted were observed. Scenarios typically involved partitioning between the vapor

phase and fog and other circumstances where water drop size was very small. In our study all precipitation collections focused on rain thus it is likely that equilibrium was achieved.

This assumption was supported by relatively close agreement between the computed median of the fraction  $\alpha$ -endosulfan in rain (concentration in rain divided by the sum of the concentrations of both endosulfan isomers) and the predicted value computed using temperature adjusted Henry's law constants and the median of fraction  $\alpha$ -endosulfan in air, 0.85 at HAA (Hapeman et al., 2013). The temperature adjusted (to the mean annual temperature, 23 °C)  $H$  was determined by using linear regression parameters determined from published measurements (Cetin et al., 2006). Inserting computed  $H$  into the equilibrium expressions for  $W_G$  and solving simultaneously for concentrations in the aqueous phase using the measured fraction  $\alpha$ -endosulfan in air, yielded a fraction  $\alpha$ -endosulfan in rain equal to 0.29. The median value determined using concentration measurements in rain samples was 0.26 (Fig. 2). The difference between the two values was small and likely within experimental error. Thus we conclude that the equilibrium expressions for  $W_G$  were applicable and that the gas phase endosulfan was likely in equilibrium with rain in samples collected.

These values were also in agreement with other published studies indicating that equilibrium partitioning between endosulfan vapor and aqueous phases is a general feature of its atmospheric washout. For example, the average fraction reported for precipitation in the Great Lakes Basin (USA) was 0.24 to 0.26 (Chan et al., 1994, 2003). In studies conducted in Belgium the fraction was 0.28 to 0.33 (Quaghebeur et al., 2004). A mean of 0.33 was computed for samples collected in the Pantanal Basin in Brazil (Laabs et al., 2002).

The lower endosulfan sulfate rate of detection and concentration in rain samples was due to correspondingly low concentrations in air. Other factors were low volatility of the degradation product and the fact that atmospheric emissions likely originated from soil surfaces where the compound was formed (Weber et al., 2010). As noted by Sarigiannis et al. (2013) under similar meteorological conditions, volatilization of pesticides from plant surfaces is up to three times higher

than from soil. The low rates of endosulfan sulfate detection and measured concentrations were consistent with reports that endosulfan exhibits relatively high photochemical stability and that formation of endosulfan sulfate is primarily due to biologically catalyzed oxidation (Weber et al., 2010). Thus, it is unlikely that either endosulfan isomer was converted to endosulfan sulfate during endosulfan atmospheric transport.

Finally, trends in observations at EVR, BNP, and HAA reflected regional rainfall patterns. Examining the stable isotopic composition ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of rainfall showed that rain near BNP was derived primarily from moisture evaporated from coastal waters and the trade wind belt of the tropical North Atlantic (Price et al., 2008). Thus it is not surprising that this site had the smallest overall rates of endosulfan detection and mean and median concentrations (Table 1). Isotope data collected within the HAA indicated that evaporated surface water from the Everglades contributed substantially to atmospheric moisture and rainfall. It follows that endosulfan detection frequencies and medians were higher since atmospheric moisture and rainfall originated within the area where endosulfan was used. The lower endosulfan levels detected in EVR samples were presumably due to the distance of this site from the area of endosulfan use.

### 3.3. Seasonal concentration trends

Seasonal patterns in endosulfan and endosulfan sulfate measurements were evaluated by dividing samples collected at each site into two groups, those collected during periods of high and low agricultural activity. The high agricultural activity season included samples collected from October through the end of April and the low agricultural activity season included those collected from May through September. These periods generally reflect the region's wet and dry seasons and the timing of vegetable production. Most crops are produced during winter months when rainfall is lowest. Fields are left fallow during the hot rainy summer months.

At all sites, greater detection frequencies of all analytes were observed in the high when compared to the low agricultural activity season; means and medians were also larger during the high agricultural activity season. This is reflected in a plot of monthly volume weighted concentrations computed by dividing the total monthly deposition by the total rainfall volume (Fig. 3). The same trends were observed when either 0 or the MDL was inserted for values reported < MDL.

Total endosulfan means and medians were significantly greater, by 2 to 10-fold, in samples collected during the high agricultural activity period (Table 2). The  $\alpha$ - and  $\beta$ -endosulfan medians were also significantly greater during the high agricultural activity period at all sites. In addition the endosulfan sulfate median at HAA was higher during the high when compared to the low agricultural activity season. The latter result may be due in part to a greater potential for wind-blown dust to be generated from soil during growing seasons due to tillage operations and a trend toward lower rainfall. As indicated endosulfan sulfate is formed in soil and its  $K_{oc}$ , about 5000 mL g<sup>-1</sup>, reflects strong binding to soil organic matter (Weber et al., 2010).

Significant differences were not indicated in medians of the fraction of  $\alpha$ -endosulfan in rain samples when data were evaluated by season and across all samples (Fig. 2). This observation appears to support the conclusion that rain scavenging of gas phase endosulfan was the primary deposition process throughout the year and that equilibrium partitioning drove the process.

### 3.4. Deposition

Total endosulfan wet deposition followed concentration patterns of the two isomers and endosulfan sulfate with the highest rates at the HAA followed by the EVR and BNP sites (Table 3). Samples collected during the high contributed more wet deposition than during the low agricultural activity season; even though rainfall during the high

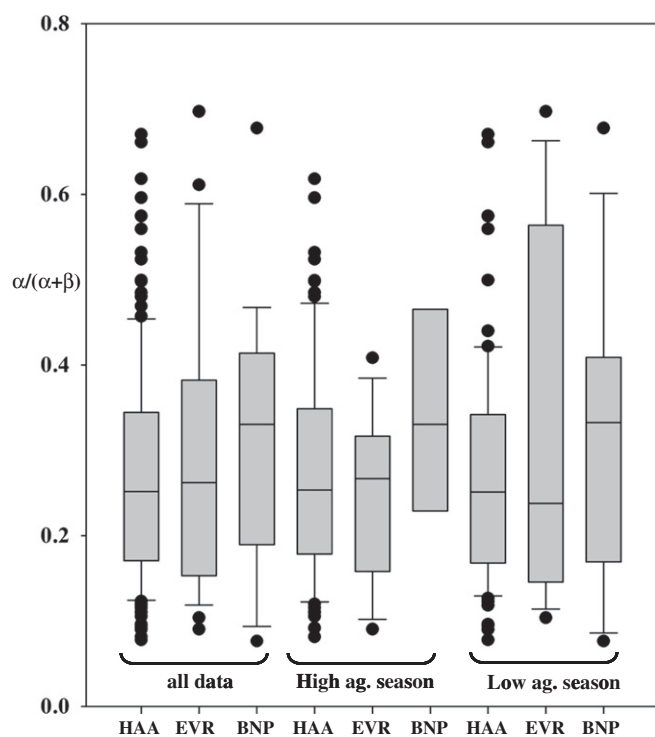


Fig. 2. Box and whisker plot of  $\alpha$ -endosulfan concentration expressed as a fraction of the sum of the  $\alpha$ - and  $\beta$ -endosulfan concentrations,  $\alpha/(\alpha + \beta)$  in rainfall samples collected at the Homestead Agricultural Area (HAA), Everglades (EVR), and Biscayne Bay (BNP) sites.

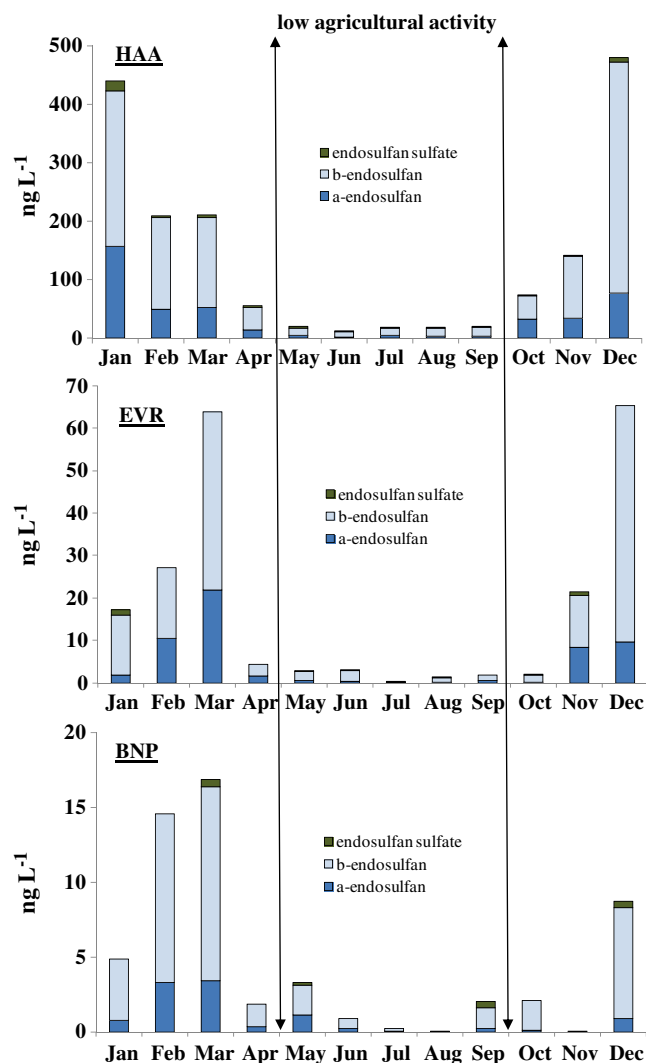


Fig. 3. Monthly volume weighted average concentration of  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate in rainfall.

agricultural activity season was less than 50% of that observed during the rainy summer season when agricultural activity was low (Table 3). The higher deposition at HAA and during periods of high agricultural activity at all sites can be explained by high HAA atmospheric endosulfan concentration measurements (Hapeman et al., 2013). Climatic factors may have also contributed. Periods of high agricultural activity occurred during winter months when atmospheric temperatures were cooler. The H of both endosulfan isomers decreases with temperature (Cetin et al., 2006) thus increasing potential for washout by rainfall. Rain storms are also less intense during this time period with smaller drop size. Both factors may have contributed to more efficient rain-drop entrapment and washout (Daly and Wania, 2005).

Total endosulfan wet deposition rates observed at EVR and BNP, 1.5 to 21  $\text{ng m}^{-2} \text{day}^{-1}$ , were consistent with results found in other areas of the continental USA where endosulfan use rates were lower and at moderate (10 to 20 km) distances from sources (Gioia et al., 2005; Goel et al., 2005; Kuang et al., 2003). For HAA, much higher daily deposition, 200  $\text{ng m}^{-2} \text{day}^{-1}$ , was calculated for the entire monitoring period and 90 and 280  $\text{ng m}^{-2} \text{day}^{-1}$  for the low and high agricultural activity periods, respectively. We are aware of only one higher published wet deposition measurement, 1500  $\text{ng m}^{-2} \text{day}^{-1}$  (Laabs et al., 2002). This deposition rate was determined using rain samples collected in the humid-tropical Pantanal Basin in Brazil during a 113 day period at a site 2 km from cotton fields. In the study area, endosulfan was applied by

Table 2

Summary statistics for total endosulfan concentration ( $\text{ng L}^{-1}$ ) by site and season.

	High agricultural activity (Oct–May)	Low agricultural activity (Jun–Sept)
<b>HAA</b>		
Number samples (% detects)	85 (98)	129 (81)
Minimum concentration	3.4	1.8
Maximum concentration	3100	890
Mean $\pm$ std <sup>a</sup>	269 $\pm$ 440	39 $\pm$ 96
KM mean $\pm$ std <sup>b</sup>	260 $\pm$ 436	33 $\pm$ 87
KM median (25th to 75th percentiles) <sup>b</sup>	130 (66 to 290)	14 (7.0 to 32)
<b>EVR</b>		
Number samples (% detects)	46 (57)	76 (36)
Minimum concentration	1.7	0.61
Maximum concentration	180	37
Mean $\pm$ std <sup>a</sup>	49 $\pm$ 52	6.4 $\pm$ 8.7
KM mean $\pm$ std <sup>b</sup>	31 $\pm$ 44	3.2 $\pm$ 5.8
KM median (25th to 75th percentiles) <sup>b</sup>	15 (2 to 38)	1.5 (0.5 to 3.0)
<b>BNP</b>		
Number samples (% detects)	86 (36)	80 (31)
Minimum concentration	1.3	0.43
Maximum concentration	110	29
Mean $\pm$ std <sup>a</sup>	18 $\pm$ 22	5.8 $\pm$ 5.9
KM mean $\pm$ std <sup>b</sup>	8.4 $\pm$ 15	2.8 $\pm$ 4.2
KM median (25th to 75th percentiles) <sup>b</sup>	3.0 (0 to 9.5)	1.5 (0 to 3.5)

The sum of  $\alpha$ -endosulfan,  $\beta$ -endosulfan and endosulfan sulfate was expressed as equivalents of endosulfan. HAA = Homestead Agricultural Area; EVR = Everglades National Park; BNP = Biscayne National Park.

<sup>a</sup> Mean  $\pm$  standard deviation of samples with measured concentration greater than the method detection limit.

<sup>b</sup> Mean  $\pm$  standard deviation and median (25th to 75th percentiles) based on Kaplan–Meier survival statistics with the insertion of method detection limits (Helsel, 2013).

aircraft, a factor which likely contributed to the very high deposition rate. Drift and volatilization losses are typically much higher with applications made with aircraft compared to tractor mounted spray systems (U.S.EPA, 2002). Endosulfan applications in the HAA were with tractor mounted booms, thus endosulfan volatilization and re-deposition although high were less than those in the Brazil study.

In addition to wet deposition, deposition of endosulfan vapor and endosulfan containing dust particles on soil surfaces likely contributed to depositional flux within HAA. No direct measures of vapor and dust deposition were made in our study. Few such measurements have been reported. Larney et al. (1999) reported dust deposition of endosulfan within 1 km in the three months following endosulfan application to a cotton field in Australia between 150 and 350  $\text{ng m}^{-2} \text{day}^{-1}$ . This is comparable to the wet deposition rates measured at the HAA site.

Table 3

Total endosulfan wet deposition summary.

	Site	Rain mm	Period <sup>a</sup> days	Daily deposition <sup>b,c</sup> $\text{ng m}^{-2} \text{day}^{-1}$
All samples	HAA	3351	1176	199–201
	EVR	2150	792	17–21
	BNP	2319	1361	1.6–2.5
Low agricultural activity period (June–Sept)	HAA	2211		87–90
	EVR	1648		9.0–15
	BNP	1305		1.4–4.2
High agricultural activity period (Oct–May)	HAA	1140		278–280
	EVR	502		23–26
	BNP	1014		3.8–5.2

The Sum of  $\alpha$ -endosulfan,  $\beta$ -endosulfan and endosulfan sulfate expressed as equivalents of endosulfan. HAA = Homestead Agricultural Area; EVR = Everglades National Park; BNP = Biscayne National Park.

<sup>a</sup> Time between 1st and last samples.

<sup>b</sup> Daily deposition equal total deposition divided by number of days.

<sup>c</sup> The lower value in the range reported for daily deposition was based on computations where zero was inserted when values were < MDL; the higher value was associated with the insertion of the detection limit for values < MDL.

Although HAA wet deposition was high when compared to most published measurements, it appeared to represent only a small fraction of endosulfan that may have volatilized during the insecticide's use for HAA crop production. Estimates of volatilization losses were computed using county level vegetable crop area estimates from the USDA 2007 Agricultural Census (USDA-NASS, 2012), estimated endosulfan use for the same period (Stone, 2013), and a 70% volatilization rate (Kennedy et al., 2001). This yielded an atmospheric emission rate of  $260,000 \text{ ng m}^{-2} \text{ day}^{-1}$ . The estimated wet deposition was about 0.1% of this value. The fate of the remaining 99.9% of the endosulfan that may have volatilized is uncertain with the exception that wet deposition measurements showed that a very small fraction, between 0.0003 and 0.007% was deposited within the two National Parks (Table 3).

Trajectory analysis conducted over a three week period in March 2005 strongly supported the conclusion that HAA emissions were the source of endosulfan wet deposition at EVR (Hapeman et al., 2013). Modeled dispersion plumes from HAA during a period of high agricultural activity indicated direct transport to the EVR. Total endosulfan wet deposition measured on this date was  $1600 \text{ ng m}^{-2}$  accounting for >12% of the total endosulfan deposited at EVR during the 2 years that the samples were collected.

Deposition during March was also greatest at all sites accounting for 29, 66, and 18% of total deposition at BNP, EVR, and HAA sites respectively. During March many of the vegetable crops produced in the region reach maturity and are harvested thus it is likely that endosulfan applications were increased to protect crop quality. High March deposition was reflected in the computed monthly volume weighted total endosulfan concentrations at EVR and BNP (Fig. 2). The high endosulfan use rate in HAA and storm trajectories that carried air masses containing endosulfan from HAA to either BNP or EVR provide a plausible explanation.

Another mechanism of endosulfan deposition in the National Park areas not accounted for in deposition with rainfall was air-surface water exchange. One set of measurements made during summer months at sites in Izmir Bay in eastern Turkey indicated that the average depositional flux of  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate was 640, 270, and  $10 \text{ ng m}^{-2} \text{ day}^{-1}$ , respectively (Odabasi et al., 2008). Reported air concentrations were  $\alpha$ -endosulfan, 4.4;  $\beta$ -endosulfan, 0.8; and endosulfan sulfate,  $0.03 \text{ ng m}^{-3}$ . Air concentrations at EVR during our measurement period were comparable averaging  $2.3 \text{ ng m}^{-3}$  for  $\alpha$ -endosulfan,  $0.4 \text{ ng m}^{-3}$  for  $\beta$ -endosulfan, and  $0.04 \text{ ng m}^{-3}$  for endosulfan sulfate (Hapeman et al., 2013). This suggests that vapor deposition may have been similar to that measured in Izmir Bay and as a result 2 to 3-fold greater than EVR wet deposition estimates (Table 3).

Endosulfan measurements made in samples collected at gate (S-178) on a freshwater canal located between the HAA and EVR sites provide some insight into potential endosulfan impact on water quality in the region and the role that atmospheric deposition might play (Fig. 1). The canal is at the edge of a buffer area between crop production areas and Everglades National Park and about mid-way between our HAA and EVR sites. The gate is typically closed thus flow and runoff from upstream areas are not common. Surface water samples were collected quarterly between 1992 and 2007 analyzed for suite of pesticides including  $\alpha$  and  $\beta$ -endosulfan and endosulfan sulfate (Pfeuffer, 2011; Rand et al., 2010). Detection frequencies for  $\alpha$ -endosulfan, 45%;  $\beta$ -endosulfan, 33%; and endosulfan sulfate, 74%, were high and at times total endosulfan concentration exceeded both the acute,  $0.22 \text{ ug L}^{-1}$  and chronic,  $0.056 \text{ ug L}^{-1}$ , water quality thresholds established for protection of freshwater organisms (Rand et al., 2010). Data also indicated relatively rapid endosulfan degradation since the endosulfan sulfate was detected most frequently and at highest concentration (Rand et al., 2010). Numerous other studies have reported that detection frequencies and concentrations in surface waters were endosulfan sulfate >  $\alpha$ -endosulfan >  $\beta$ -endosulfan and emphasized that there are several factors that may account for this (Weber et al., 2010).

### 3.5. Potential for ecological impact

Potential ecosystem effects due to endosulfan presence in rain samples were assessed by comparing total endosulfan concentrations in rain samples to freshwater acute and chronic water quality criteria (Fig. 4). HAA samples exceeded the acute threshold,  $0.22 \text{ ug L}^{-1}$ , in 16% of samples and the chronic threshold,  $0.056 \text{ ug L}^{-1}$ , in 42%. The samples collected during the high agricultural activity period in winter 2005–2006 were notable since many exceeded the acute threshold by 10 to 15-fold. This presumably was during a period of intense endosulfan use. None of EVR and BNP sample concentrations exceeded the acute threshold while 4% exceeded the chronic exposure threshold. At BNP concentrations were lowest compared to other sites. Aquatic organisms are unlikely to be exposed to concentrations present in rainwater due to dilution after deposition; nevertheless data show that wet deposition is a mechanism for endosulfan transport to remote areas within the National Parks and that risks are indicated. The highest risk was most likely for organisms that dwell in shallow ponds and wetlands. Many of the habitats within the Everglades ecosystem fit into these categories (Rand et al., 2010).

Another characteristic of the data was that endosulfan depositional fluxes were highly episodic. For example, the deposition during the two highest events at EVR, BNP, and HAA yielded 44, 33, and 16% of the total endosulfan deposition at these sites over the entire monitoring period. These events coincided with peak concentrations and indicated potential for high short term exposures.

A related concern is that long-term endosulfan deposition at remote locations within the National Parks could result in the accumulation of toxic residues in sediments and bioaccumulation in fish and other organisms. Rand et al. (2010) summarized detections of endosulfan residues in fish captured within Everglades National Park. Detections in whole body samples exceeded 90th centile concentration estimates in 60% of samples analyzed. The principal form of endosulfan detected was the toxic degradate, endosulfan sulfate. Wet and dry deposition of

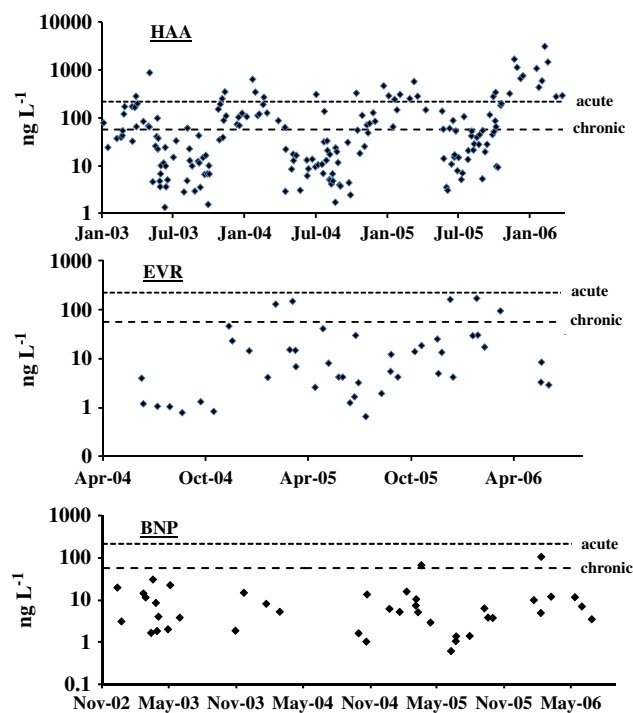


Fig. 4. Sum of  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate concentrations in rain samples collected at the Homestead Agricultural Area (HAA), Everglades (EVR), and Biscayne Bay (BNP) sites with measured values greater than method detection limits compared to acute and chronic toxicity thresholds for freshwater organisms (U.S.EPA, 2012).



endosulfan may be its source since oxidative degradation in soil, sediment, and water results in its production from the parent compound. Sediment accumulation and persistence has also been noted (Weber et al., 2010).

Finally, deposition measurements indicated that only a small fraction, <0.1%, the endosulfan that may have volatilized after application was accounted for. The fate of remaining material is unknown.

#### 4. Conclusions

The two isomers of endosulfan and its degradate, endosulfan sulfate, were detected at high frequency in event-based rain samples within an area of high endosulfan use in southern Florida and in two nearby National Parks. The highest concentrations and deposition rates were in samples collected within the agricultural area. Strong seasonal trends in data were observed at all sites with detection frequencies and median concentrations 2 to 9-fold greater during periods of high agricultural activity. This supports the conclusion that the principal endosulfan source in rain samples was from local use. The relatively high deposition in the crop production area and frequency of observation at all sites of concentrations that exceeded aquatic life toxic effect thresholds indicated that endosulfan wet deposition may be an ecotoxicological concern in the region. The magnitude of deposition measurements may also explain the frequent detection of endosulfan residues in fish tissue and sediments at sites not adjacent to crop production areas (Rand et al., 2010). In addition, the high deposition measurements made at HAA and those reported by Laabs et al. (2002) indicate that humid tropical and/or sub-tropical climatic conditions may be a strong driver in promoting endosulfan volatilization and re-deposition in rainfall and by other mechanisms. This emphasizes a need for further studies to assess modes of transport of endosulfan and other semi-volatile pesticides in South Florida and other regions with similar climate and crop production practices.

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